Supporting Information

Rhenium(I) Tricarbonyl Complexes with Peripheral *N*-Coordination Sites: a Foundation for Heterotrimetallic Nonlinear Optical Chromophores

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1. Additional Crystallographic Data

Table S1. Crystallographic Data and Refinement Details for Solvates of 1–6

	1·Me_2CO	**2**·PhMe	**3**·0.5PhMe	**4**·0.5Me_2CO	**5**·0.5PhMe	**6**·MeCN
empirical formula	$C_{18}H_{12}ClN_4O_4Re$	$C_{25}H_{17}F_3N_5O_6ReS$	$C_{24.5}H_{15}F_3N_5O_6ReS$	$C_{23.5}H_{13}F_3N_6O_{6.5}ReS$	$C_{31}H_{18}ClN_4O_3Re$	$C_{32}H_{20}F_3N_6O_6ReS$
fw	569.97	758.70	750.67	758.66	716.14	859.80
cryst system	monoclinic	triclinic	orthorhombic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	*Pbcn*	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	6.7065(4)	9.8664(5)	20.920(1)	10.602(1)	7.0510(8)	14.9062(5)
b/Å	24.786(1)	10.8251(6)	14.1928(6)	12.0951(9)	23.671(3)	15.4034(4)
c/Å	12.0178(6)	13.6341(7)	18.5858(8)	12.4270(8)	15.021(2)	16.6113(5)
a/deg	90.00	70.788(5)	90	89.784(6)	90	90
β/deg	100.237(5)	80.269(4)	90	66.738(8)	92.193(9)	102.651(3)
γ/deg	90.00	76.658(4)	90	67.606(8)	90	90
U/Å^3	1965.8(2)	1331.1(1)	5518.3(4)	1333.2(2)	2505.2(5)	3721.5(2)
Z	4	2	8	2	4	4
T/K	101(2)	100(2)	150(2)	150(2)	150(2)	150(2)
μ/mm^{-1}	6.349	4.715	4.548	4.709	5.001	3.383
cryst size/mm	0.1 × 0.1 × 0.05	0.4 × 0.2 × 0.05	0.1 × 0.02 × 0.02	0.25 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.35 × 0.08 × 0.08
cryst description	red rhombohedron	yellow plate	orange needle	light red needle	light yellow block	yellow needle
reflns collected	6760	9086	15277	8303	14375	13112
independent reflns (R_{int})	3596 (0.0494)	5640 (0.0389)	5876 (0.0567)	4838 (0.0445)	5108 (0.1352)	7541 (0.0412)
θ_{max}/deg (completeness)	25.35 (99.9)	26.73 (99.7)	28.64 (99.3)	25.35 (99.1)	26.37 (99.8)	26.38 (99.4)
reflns with $I > 2\sigma(I)$	2824	5103	3534	4013	2889	5604
GOF on F^2	1.099	1.080	1.104	1.047	0.948	1.070
final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0544, 0.1145	0.0381, 0.0808	0.0527, 0.0749	0.0472, 0.0762	0.0751, 0.0975	0.0586, 0.1494
(all data)	0.0753, 0.1249	0.0441, 0.0865	0.1122, 0.1013	0.0639, 0.0853	0.1554, 0.1240	0.0844, 0.1679
peak and hole/eÅ^{-3}	2.82, –1.39	2.12, –2.20	2.27, –1.25	1.11, –0.86	1.26, –0.88	4.68, –1.62

2. Additional ^{1}H NMR Spectroscopic Data

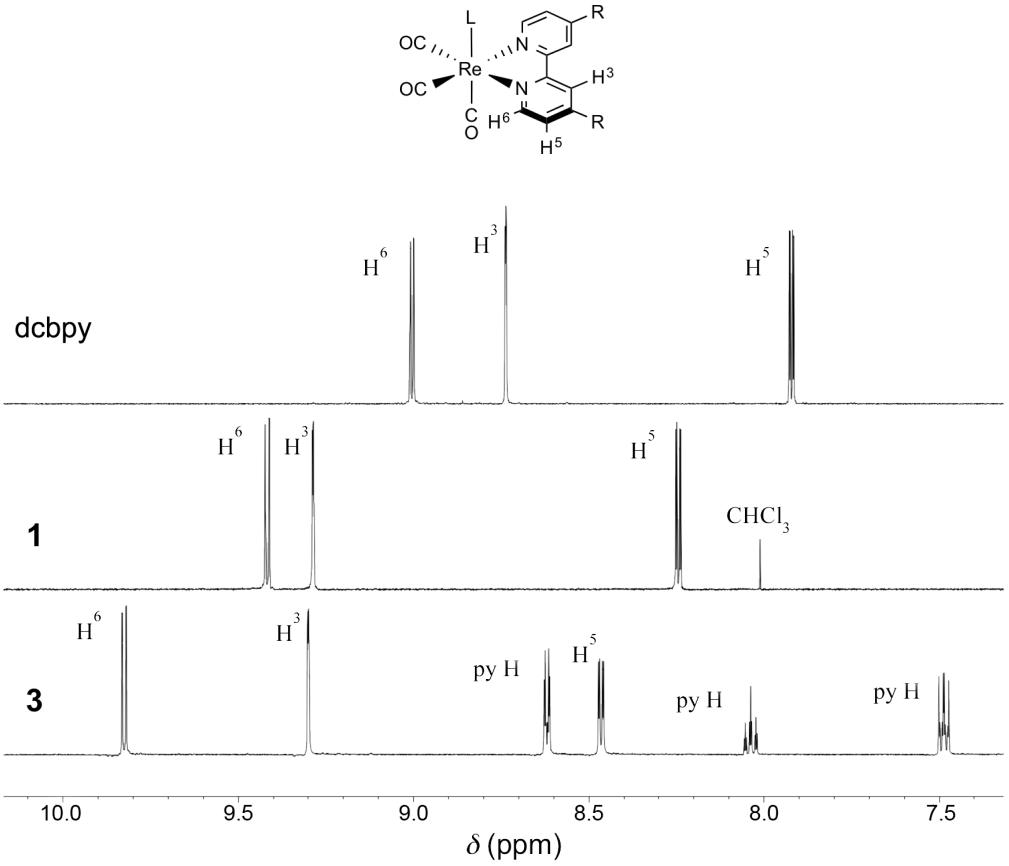

Figure S1. ^{1}H NMR spectra of dcbpy, **1** and **3** (500 MHz in $(CD_3)_2CO$ at 293 K). Complexing to a *fac*-Re^{I}Cl(CO)$_3$ center induces large downfield shifts of all signals, while substituting the Cl^- ligand with py causes further such shifts, although that for the H^3 signal is only slight.

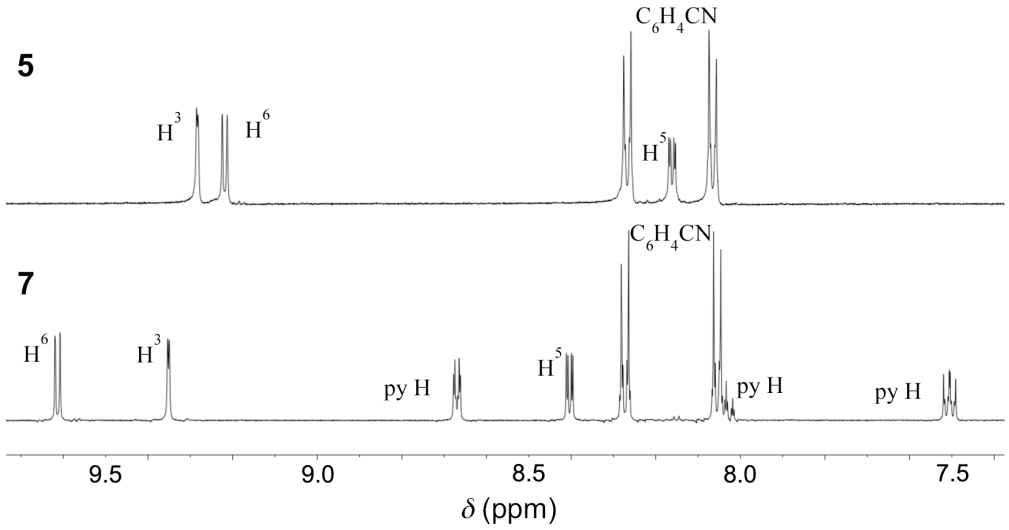

Figure S2. ^{1}H NMR spectra of **5** and **7** (500 MHz in $(CD_3)_2CO$ at 293 K). Replacing the Cl^- ligand with py shifts the signals for the bpy unit downfield (especially the H^5 and H^6 signals), while those for the benzonitrile fragments are essentially invariant.

3. Additional Electrochemical and Spectroelectrochemical Data

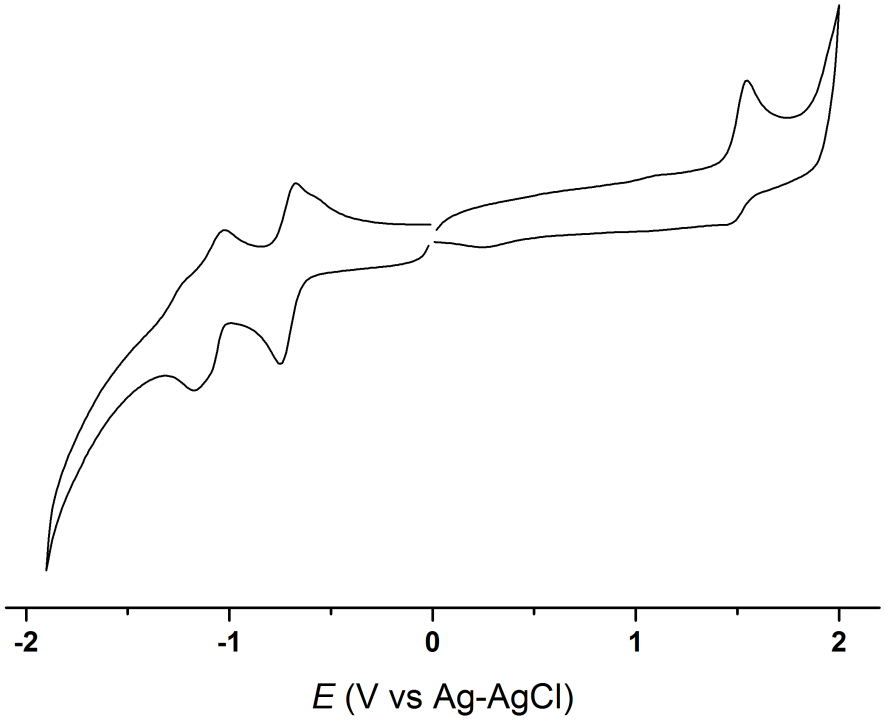

Figure S3. Cyclic voltammogram of complex **1** recorded at 100 mV s^{-1} in MeCN 0.1 M in $[N(C_4H_9\text{-}n)_4]PF_6$ at 293 K.

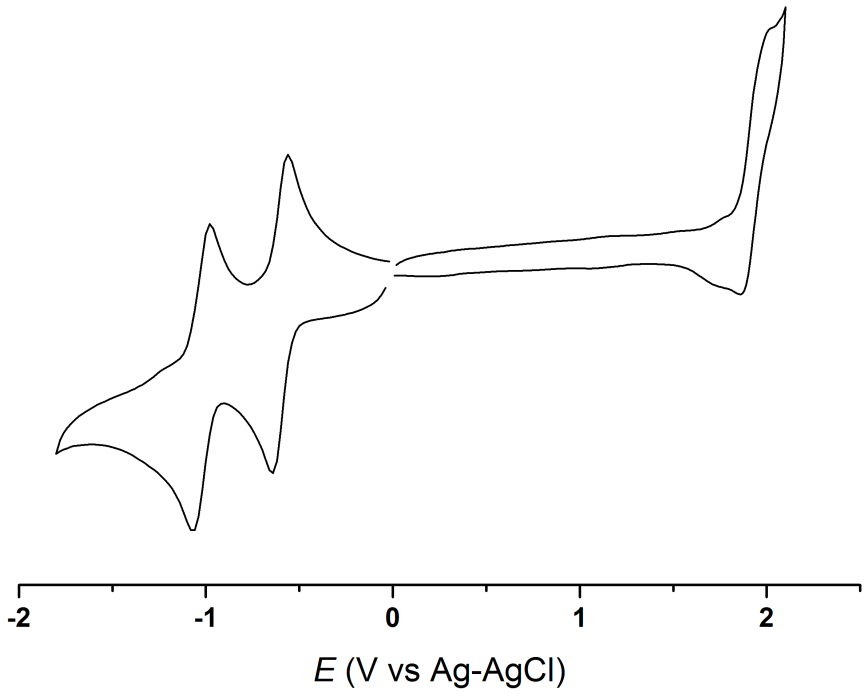

Figure S4. Cyclic voltammograms of complex salt **2** recorded at 100 mV s^{-1} in MeCN 0.1 M in $[N(C_4H_9\text{-}n)_4]PF_6$ at 293 K.

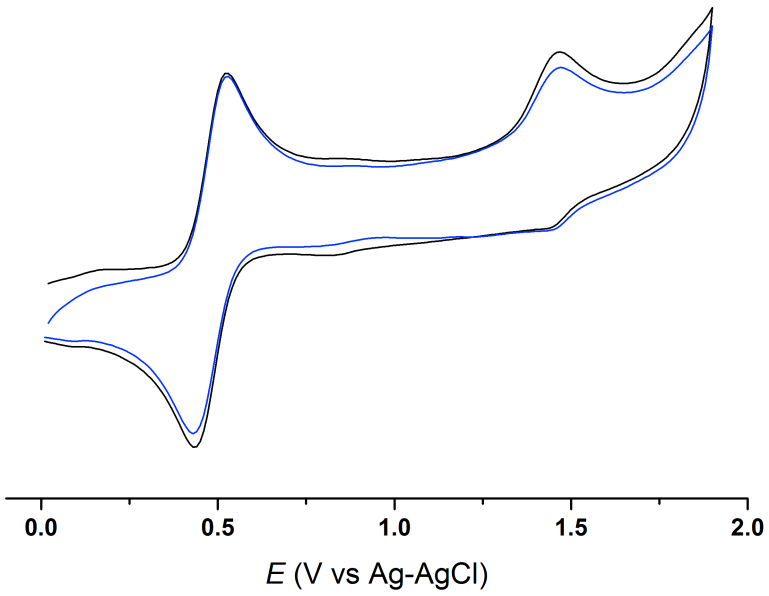

Figure S5. Cyclic voltammograms depicting the 1st (black) and 2nd (blue) scan for the oxidation processes of complex salt **11** recorded at 100 mV s^{-1} in MeCN 0.1 M in $[N(C_4H_9\text{-}n)_4]PF_6$ at 293 K.

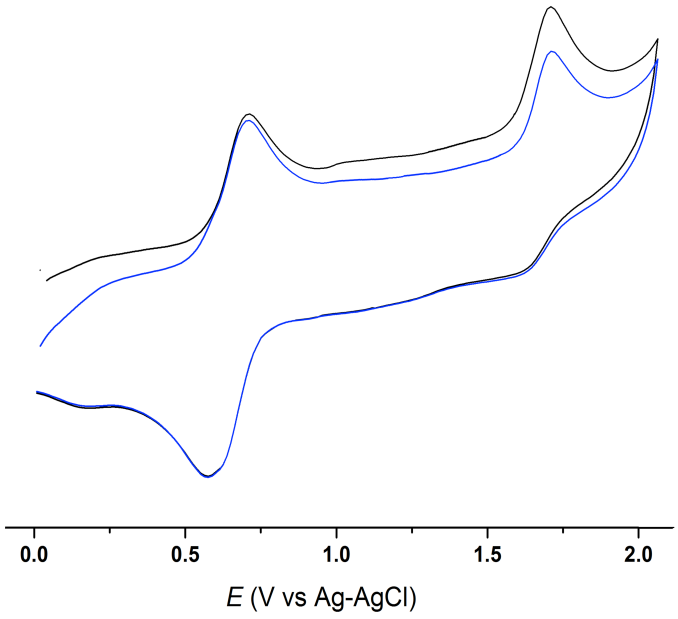

Figure S6. Cyclic voltammograms depicting the 1st (black) and 2nd (blue) scan for the oxidation process of complex salt **12** recorded at 100 mV s^{-1} in MeCN 0.1 M in $[N(C_4H_9\text{-}n)_4]PF_6$ at 293 K.

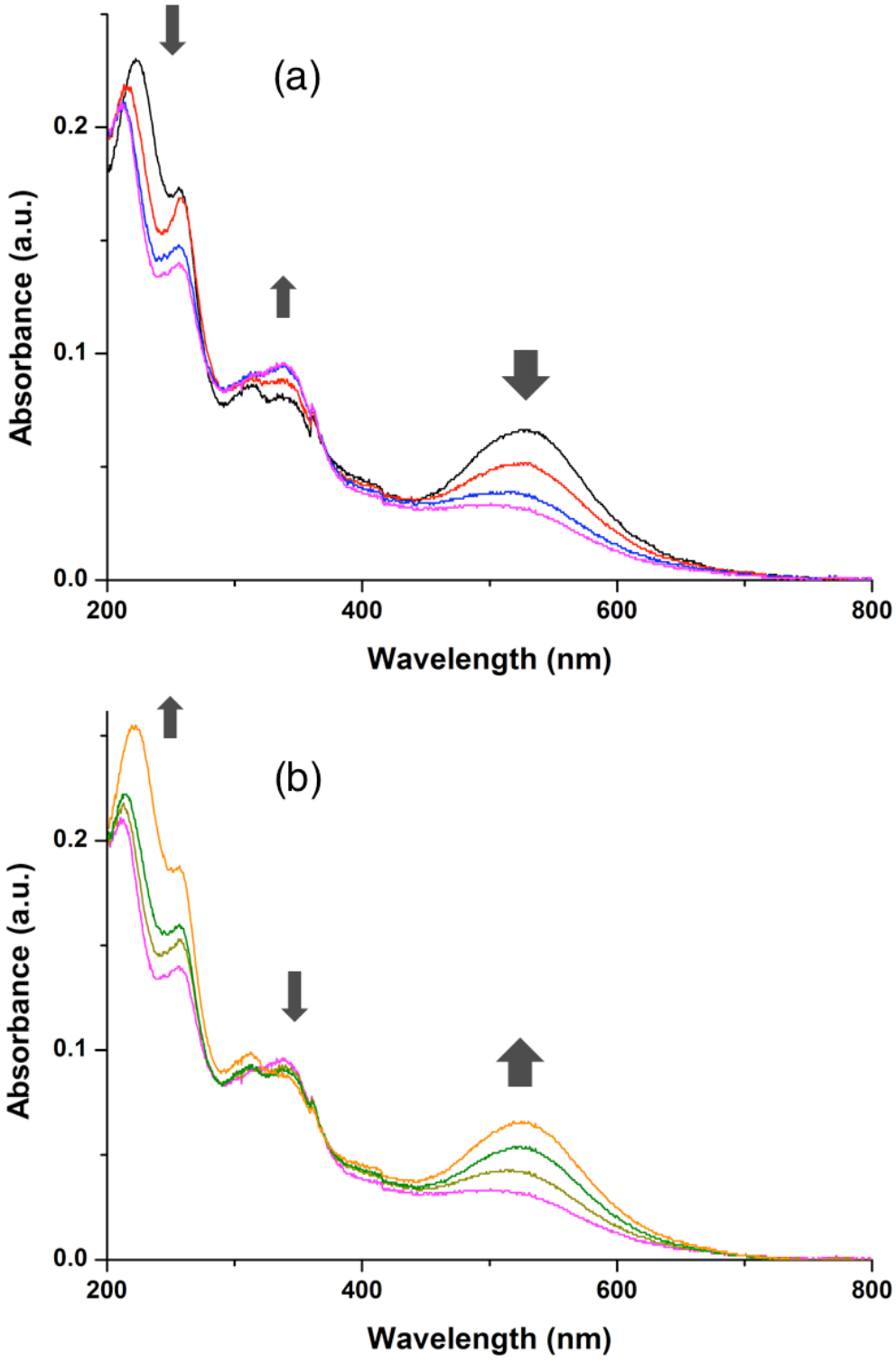

Figure S7. Spectroscopic changes upon oxidation at 1.0 V vs Ag–AgCl (a) followed by reduction at 0.0 V (b) of complex salt **11** (ca. 10^{-4} M) in MeCN 0.1 M in $[N(C_4H_9\text{-}n)_4]PF_6$ at 293 K in an OTTLE cell.

4. Additional Electronic Absorption and Emission Spectroscopic Data

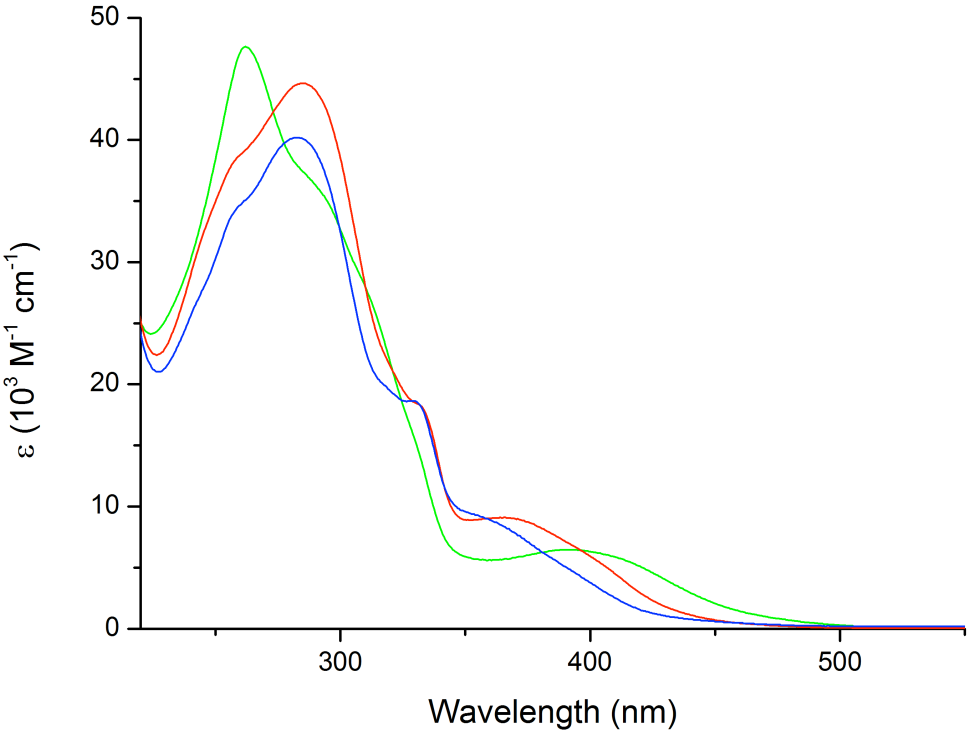

Figure S8. UV–vis absorption spectra of **5** (green), **6** (blue) and **7** (red) in MeCN at 293 K.

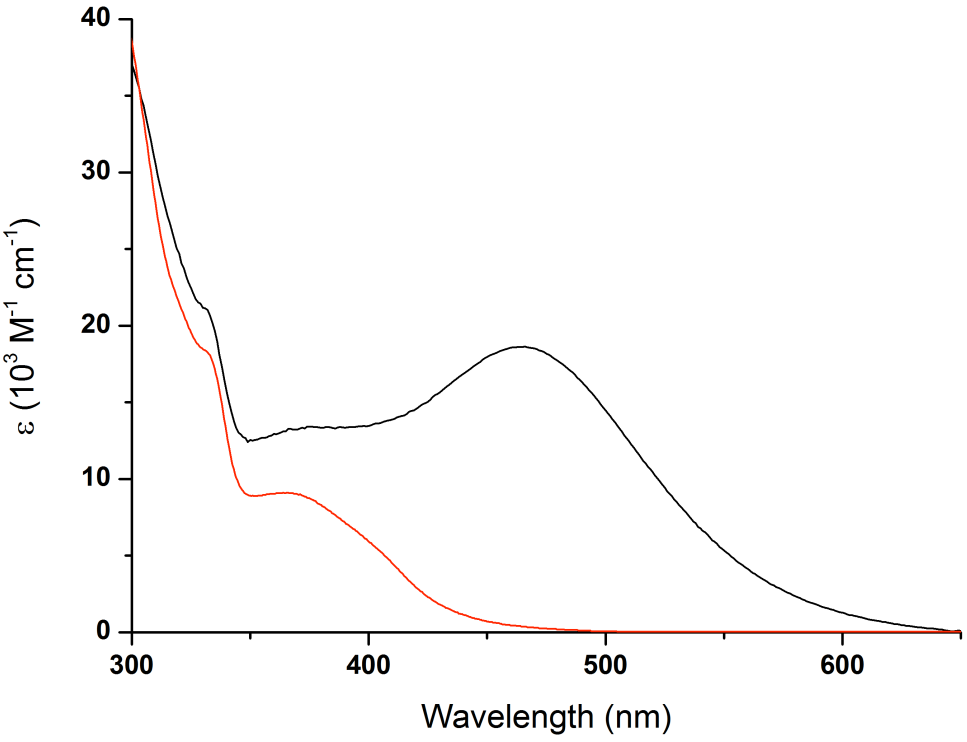

Figure S9. UV–vis absorption spectra of **7** (red) and **12** (black) in MeCN at 293 K.

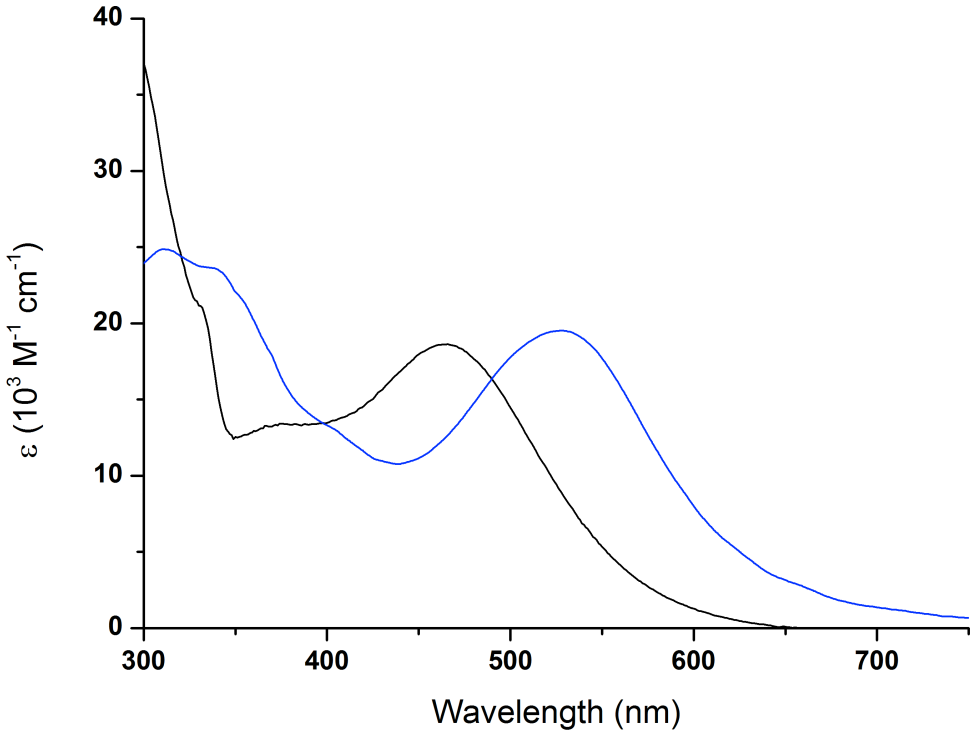

Figure S10. UV–vis absorption spectra of **11** (blue) and **12** (black) in MeCN at 293 K.

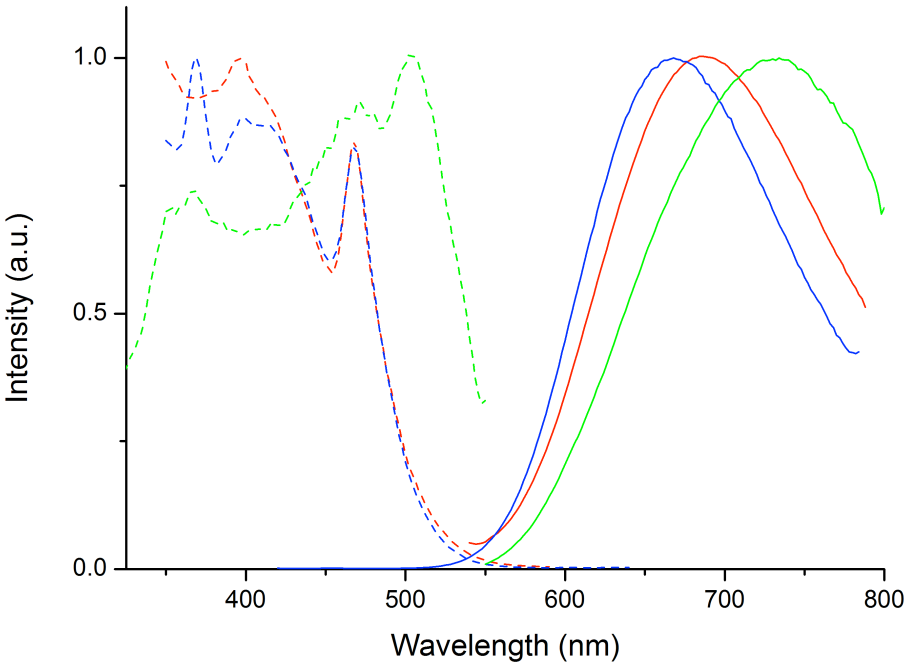

Figure S11. Emission (full lines) and excitation (dashed lines) spectra of the dcbpy-containing complex salts **2** (blue), **3** (green) and **4** (red) recorded in MeCN at 293 K.

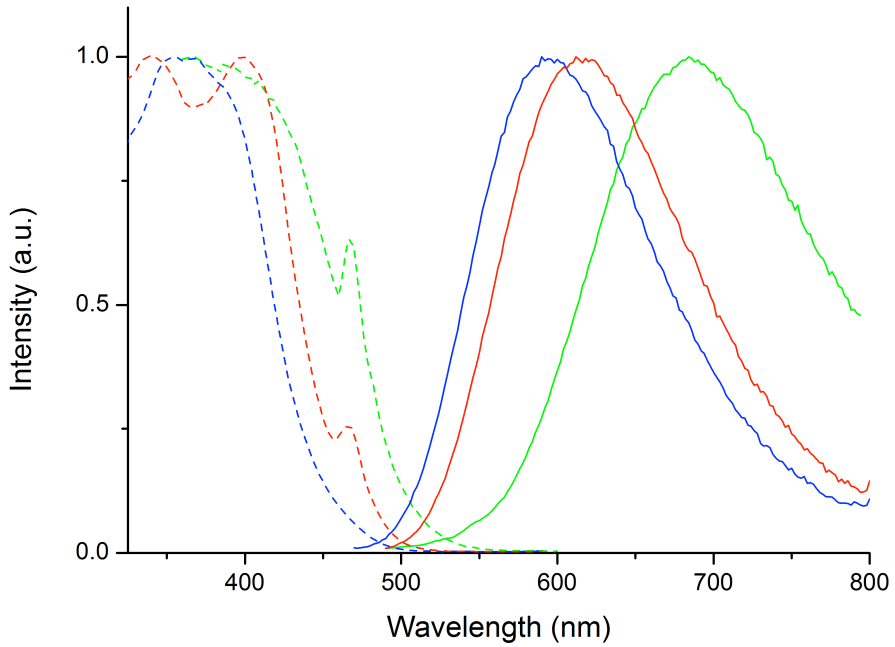

Figure S12. Emission (full lines) and excitation (dashed lines) spectra of the bcpbpy-containing complex salts **5** (green), **6** (blue) and **7** (red) recorded in MeCN at 293 K.

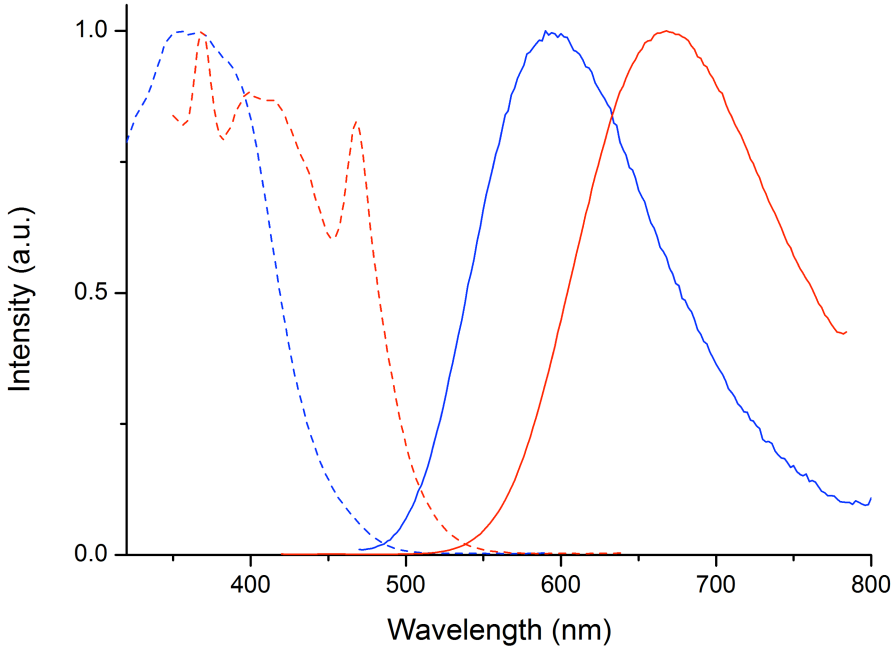

Figure S13. Emission (full lines) and excitation (dashed lines) spectra of the MeCN-containing complex salts **2** (red) and **6** (blue) recorded in MeCN at 293 K.

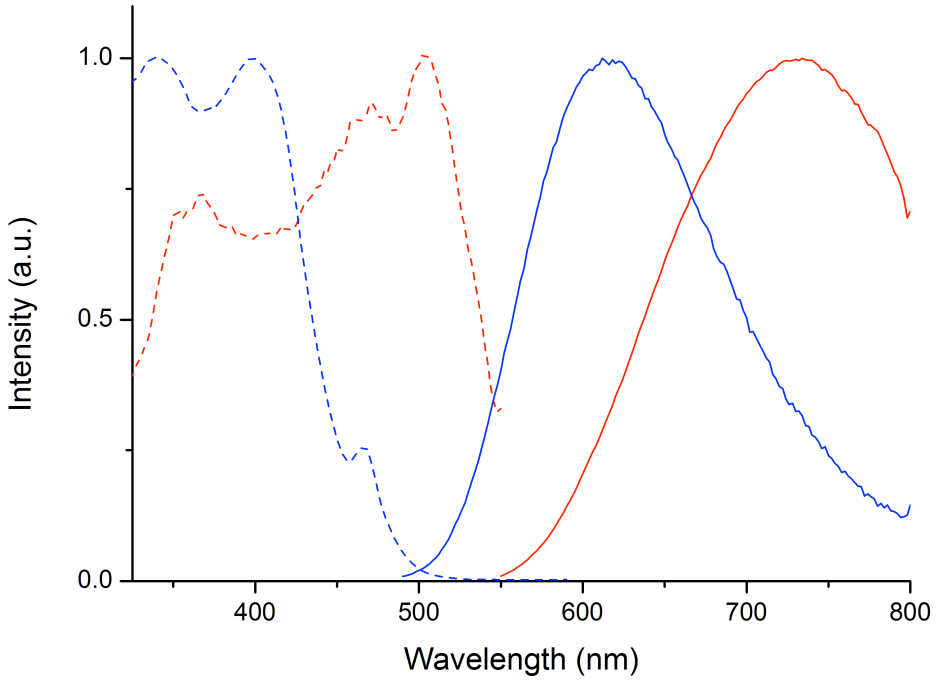

Figure S14. Emission (full lines) and excitation (dashed lines) spectra of the py-containing complex salts **3** (red) and **7** (blue) recorded in MeCN at 293 K.

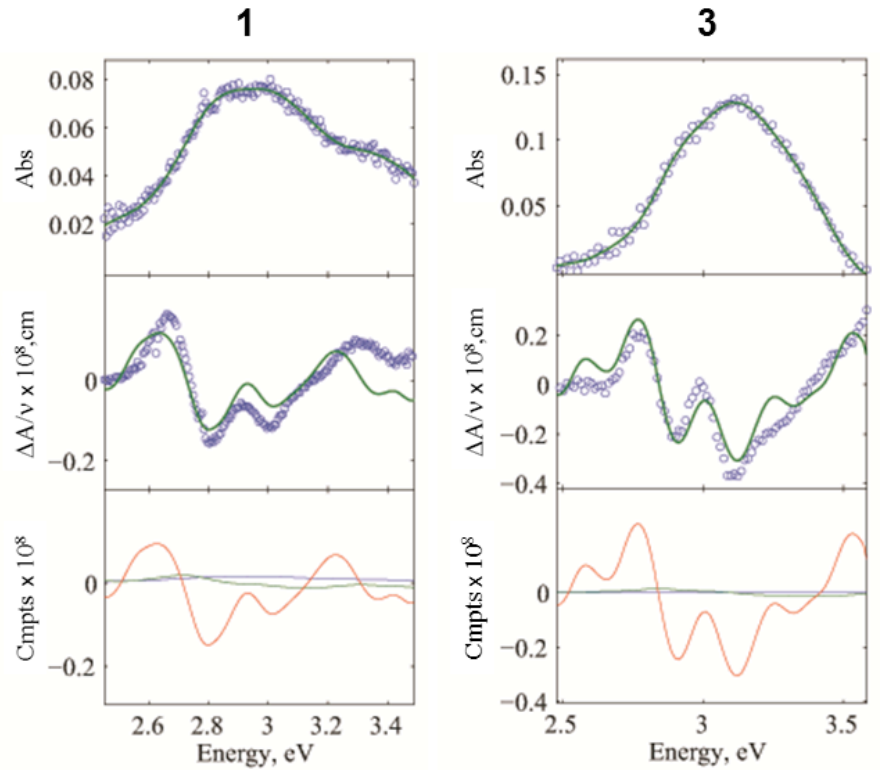

Figure S15. Spectra and calculated fits for the compounds **1** and **3** in PrCN at 77 K. Top panel: absorption spectrum; middle panel: electroabsorption spectrum, experimental (blue) and fits (green) according to the Liptay equation (Liptay, W. In *Excited States*, Vol. 1; Lim, E. C., Ed.; Academic Press, New York, 1974, pp. 129–229); bottom panel: contribution of 0th (blue), 1st (green) and 2nd (red) derivatives of the absorption spectrum to the calculated fits.